

学校编码: 10384  
学号: 20520121151468

分类号 \_\_\_\_\_ 密级 \_\_\_\_\_  
UDC \_\_\_\_\_

厦 门 大 学

硕 士 学 位 论 文

基于化学反应的二乙基磷酰氯、亚铜离子及次氯酸荧光分子探针初步研究

The molecular probes based on chemodosimeter for DCP,  
 $\text{Cu}^+$  and  $\text{HClO}$

胡潇潇

指导教师姓名: 郑 洪 副教授

专 业 名 称: 分 析 化 学

论文提交日期: 2015 年 5 月

论文答辩时间: 2015 年 5 月

学位授予日期: 2015 年 月

答辩委员会主席: \_\_\_\_\_

评 阅 人: \_\_\_\_\_

2015 年 5 月

**The molecular probes based on chemodosimeter for DCP,  
 $\text{Cu}^+$  and  $\text{HClO}$**

A Dissertation Submitted for the Degree of  
Master of Science

By

**Xiaoxiao Hu**

**Supervisor: Associate Prof. Hong Zheng**

Department of Chemistry, Xiamen University

May 2015

## 厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为 ( ) 课题(组)的研究成果,获得 ( ) 课题(组)经费或实验室的资助,在 ( ) 实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明)。

声明人(签名):

年 月 日

## 厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（        ） 1. 经厦门大学保密委员会审查核定的保密学位论文，  
于        年        月        日解密，解密后适用上述授权。

（        ） 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人：

年        月

厦门大学博硕士论文摘要库

## 摘要

荧光分子探针即是可以将物质的化学信息转换为可测量的荧光信号的一种光学传感器，它具有选择性好、灵敏度高、操作简便、实时快速检测等优点。随着相关技术的成熟，将荧光分子探针与细胞显微成像结合的技术已经成为了人类探测微观生命系统的一种重要手段。本文在前人研究的基础上，成功设计合成了三种荧光分子探针，体现了不同的检测性能。本论文共分四章，分别包括以下内容：

第一章，绪论。首先介绍了光学分子传感器的基本概念、研究现状和发展趋势，着重介绍了荧光分子探针的设计机理；其次重点介绍了神经毒剂类似物二乙基磷酰氯、亚铜离子和次氯酸荧光分子探针的研究现状和发展趋势；最后，通过结合相关文献的研究内容及本课题组工作成果，提出了本论文的研究设想。

第二章，成功设计合成以氨基花菁为母体，羧基为识别位点的二乙基磷酰氯荧光分子探针。氨基花菁本身有较大斯托克位移，我们通过二乙基磷酰氯与识别位点的反应促进分子内酰胺化反应而改变氮原子的电子云密度，进而改变该分子探针的光学性质。该探针的大斯托克位移有效避免了花菁染料的自吸收现象。该探针还有以下特点：反应速度快，检测灵敏度高，且可用于肉眼检测。

第三章，设计合成一种香豆素衍生物作为检测亚铜离子的荧光探针。亚铜离子的存在可催化探针的叠氮基和端炔基发生分子内 Click 反应，使荧光显著增强，以实现亚铜离子的荧光传感。该探针分子为设计相关亚铜离子荧光探针开辟了一条新的思路。

第四章，基于次氯酸氧化脱脒机制设计合成一种罗丹明 B 内酰脒-丹磺酰脒衍生物作为检测次氯酸的荧光探针。当有次氯酸存在时，酰脒断裂，生成罗丹明 B，同时释放出丹磺酰脒荧光团，不仅实现了比色传感，也实现了双波长荧光发射。

关键词：荧光分子探针；二乙基磷酰氯；亚铜离子；次氯酸

厦门大学博硕士论文摘要库

## Abstract

Fluorescence molecular probe is a kind of optical sensor which can transform the chemical information of substance into measurable fluorescent signal. It has the advantages of good selectivity, high sensitivity, simple operation and rapid detection in real time. And the technology of combining fluorescence molecular probe with the cell microscopic imaging has become an important means of studying the microscopic system of life. In this paper, three kinds of fluorescent molecular probes were successfully designed and synthesized on the basis of predecessors' research, which exhibited different detection properties. And this paper consists of four chapters summarized as follows:

In chapter 1 first, there is an introduction to the basic concept, current research and development trend of optical molecular sensors. Emphasis was focused on the developments of fluorescent molecular probes for diethyl phosphoryl chloride, cuprous ion and hypochlorous acid. Finally, the objective of this dissertation was proposed by combining relevant research and the work of our group.

In chapter 2, a novel fluorimetric and visual probe based on aminocyanine derivatives for highly selective detection of nerve agent simulant DCP was reported. The detection method was developed based on the intramolecular N-alkylation reaction which could reduce the electron density of nitrogen atom. The decrease of electron density would lead to a red-shift of absorption spectrum, and the increase of absorbance, as well as the fluorescence intensity. The probe had the following features: fast response, high detection sensitivity. What is more important, it also could select DCP by naked eyes.

In chapter 3, based on the Click chemistry of azide-alkyne cycloaddition, a novel



probe for detecting cuprous ion derivatives was designed and synthesised successfully. The probe achieved an “ on-off ” fluorescence response to cuprous ion in water which also opened up a new train of thought for the related design of detecting cuprous ion with fluorescent probes.

In chapter 4, a rhodamine B- dansyl derivative was designed as a fluorescent probe to detect hypochlorous acid which based on the hypochlorite oxidation mechanism. In the presence of hypochlorous acid, the hydrazide sturcure fractured and leaded to the release of fluorophore rhodamine B and dansyl derivative. The probe not only achieved the change of color from colorless to pink, but also had realized the double emission wavelength of fluorescence.

Keywords: Molecular Probes; Diethyl Phosphoryl Chloride; Cuprous Ion; Hypochlorous Acid.

摘要.....	I
Abstract.....	III
目录.....	V
Contents.....	VIII
<b>第一章 绪论</b> .....	1
<b>第一节 光学分子传感器简介</b> .....	1
1.1.1 光学分子传感器的概述.....	1
1.1.2 光学分子传感器的设计原理.....	2
1.1.3 荧光分子传感器.....	3
<b>第二节 二乙基磷酰氯荧光分子探针研究现状</b> .....	5
1.2.1 引言.....	5
1.2.2 基于罗丹明螺环结构的 DCP 荧光分子探针.....	6
1.2.3 基于亲核反应的 DCP 荧光分子探针.....	8
1.2.4 基于其他不可逆化学反应的 DCP 荧光分子探针.....	11
<b>第三节 亚铜离子荧光分子探针研究现状</b> .....	13
1.3.1 引言.....	13
1.3.2 基于络合作用的亚铜离子荧光分子探针.....	14
1.3.3 基于不可逆化学反应的亚铜离子荧光分子探针.....	16
<b>第四节 次氯酸荧光分子探针研究现状</b> .....	18
1.4.1 引言.....	18
1.4.2 基于次氯酸氧化机制的荧光分子探针.....	19
<b>第五节 论文设想与目标</b> .....	24
<b>参考文献</b> .....	25
<b>第二章 氨基花菁对二乙基磷酰氯的识别与传感</b> .....	35
<b>第一节 设计思路</b> .....	35

<b>第二节 探针分子的合成与表征</b>	36
2.2.1 仪器	36
2.2.2 试剂	36
2.2.3 探针分子的合成与表征	36
<b>第三节 实验结果与讨论</b>	40
2.3.1 实验方法	40
2.3.2 结果与讨论	40
2.3.2.1 光谱特征	40
2.3.2.2 实验条件的优化	41
2.3.2.3 动力学及稳定性	44
2.3.2.4 选择性	45
2.3.2.5 滴定曲线和工作曲线的测定	46
2.3.2.6 机理探讨与验证	48
2.3.3 结论	51
<b>本章小结</b>	51
<b>参考文献</b>	52
<b>第三章 基于 Huisgen-Click 反应对亚铜离子的识别与传感</b>	54
<b>第一节 设计思路</b>	54
<b>第二节 探针分子的合成与表征</b>	55
3.2.1 仪器	55
3.2.2 试剂	55
3.2.3 探针分子的合成与表征	55
<b>第三节 实验结果与讨论</b>	68
3.3.1 实验方法	68
3.3.2 结果与讨论	69
3.3.2.1 光谱特征	69
3.3.2.2 实验条件的优化	69
3.3.2.3 动力学及稳定性	73
3.3.2.4 选择性	74

3.3.2.5 共存离子的作用.....	75
3.3.2.6 滴定曲线和工作曲线的测定.....	75
3.3.3 结论.....	76
<b>本章小结</b> .....	76
<b>参考文献</b> .....	77
<b>第四章 基于磺酰肼氧化脱肼机制对次氯酸的识别与传感</b> .....	78
<b>第一节 设计思路</b> .....	78
<b>第二节 探针分子的合成与表征</b> .....	79
4.2.1 仪器.....	79
4.2.2 试剂.....	79
4.2.3 探针分子的合成与表征.....	79
4.2.4 其他活性氧溶液的配制.....	82
<b>第三节 实验结果与讨论</b> .....	83
4.3.1 实验方法.....	83
4.3.2 结果与讨论.....	83
4.3.2.1 光谱特征.....	83
4.3.2.2 实验条件的优化.....	85
4.3.2.3 动力学及稳定性.....	88
4.3.2.4 选择性.....	89
4.3.2.5 滴定曲线和工作曲线的测定.....	90
4.3.2.6 机理探讨.....	91
4.3.3 结论.....	93
<b>本章小结</b> .....	93
<b>参考文献</b> .....	93
<b>硕士阶段科研成果</b> .....	94
<b>致谢</b> .....	95

## Contents

<b>Abstract in Chinese</b> .....	I
<b>Abstract in English</b> .....	III
<b>Contents in Chinese</b> .....	V
<b>Contents in English</b> .....	VIII
<b>Chapter 1 Introduction</b> .....	1
<b>1.1 Brief introduction of optical molecular chemosensors</b> .....	1
1.1.1 Summarization of optical molecular chemosensors.....	1
1.1.2 Basic principles of designing optical molecular chemosensors.....	2
1.1.3 Fluorescent molecular chemsensors.....	3
<b>1.2 Research progress on fluorescent chemosensors for diethyl chlorophosphate</b> .....	5
1.2.1 Introduction.....	5
1.2.2 Fluorescent molecular chemosensors for diethyl chlorophosphate based on the action of Rhodamine.....	6
1.2.3 Fluorescent molecular chemosensors for diethyl chlorophosphate based on the nucleophilic reaction.....	8
1.2.4 Fluorescent molecular chemosensors for diethyl chlorophosphate based on irreversible and specific reactions.....	11
<b>1.3 Research progress on fluorescent chemosensors for cuprous ion</b> .....	13
1.3.1 Introduction.....	13
1.3.2 Fluorescent molecular chemosensors for cuprous ion based on the coordination of cuprous ion to the chelating ligand.....	14
1.3.3 Fluorescent molecular chemosensors for cuprous ion based on irreversible and specific reactions.....	16
<b>1.4 Research progress on fluorescent chemosensors for hypochloric acid</b> .....	18

1.4.1 Introduction.....	18
1.4.2 Fluorescent molecular chemosensors for hypochloric acid based on the oxidizing property of hypochloric acid.....	19
<b>1.5 The objective of this dissertation.....</b>	<b>24</b>
<b>References.....</b>	<b>25</b>
 <b>Chapter 2 Recognition and sensing of diethyl chlorophosphate with 4-amino butyric acid-substituted tricarbo-cyanine.....</b>	
<b>2.1 Basic idea about the design of the probe molecule.....</b>	<b>35</b>
<b>2.2 Synthesis and characterization of the probe molecule.....</b>	<b>36</b>
2.2.1 Apparant.....	36
2.2.2 Reagents.....	36
2.2.3 Synthesis and characterization of the probe molecule.....	36
<b>2.3 Results and discussion.....</b>	<b>40</b>
2.3.1 Experimental.....	40
2.3.2 Results and discussion.....	40
2.3.2.1 Spectral characteristic.....	40
2.3.2.2 Optimization of experimental conditions.....	41
2.3.2.3 Dynamic and stability.....	44
2.3.2.4 Selectivity.....	45
2.3.2.5 Calibration graphs.....	46
2.3.2.6 Discussion about the mechanism.....	48
2.3.3 Conclusion.....	51
<b>Summary.....</b>	<b>51</b>
<b>References.....</b>	<b>52</b>
 <b>Chapter 3 Recognition and sensing of cuprous ion based on the Huisgen-Click reaction.....</b>	
<b>3.1 Basic idea about the design of the probe molecule.....</b>	<b>54</b>
<b>3.2 Synthesis and characterization of the sensor molecule.....</b>	<b>55</b>

3.2.1 Apparants.....	55
3.2.2 Reagents.....	55
3.2.3 Synthesis and characterization of the probe molecule.....	55
<b>3.3 Results and discussion.....</b>	<b>68</b>
3.3.1 Experimental.....	68
3.3.2 Results and discussion.....	69
3.3.2.1 Spectral characteristics.....	69
3.3.2.2 Optimization of experimental conditions.....	69
3.3.2.3 Dynamic and stability.....	73
3.3.2.4 Selectivity.....	74
3.3.2.5 Selectivity of concomitant ions.....	75
3.3.2.6 Calibration graphs.....	75
3.3.3 Conclusion.....	76
<b>Summary.....</b>	<b>76</b>
<b>References.....</b>	<b>77</b>
 <b>Chapter 4 Recognition and sensing of hypochloric acid with Rhodamine B hydrazide.....</b>	 <b>78</b>
4.1 Basic idea about the design of the probe molecule.....	78
4.2 Synthesis and characterization of the probe molecule.....	79
4.2.1 Apparants.....	79
4.2.2 Reagents.....	79
4.2.3 Synthesis and characterization of the sensor molecule.....	79
4.2.4 Preparation of other reactive oxygen species.....	82
<b>4.3 Results and discussion.....</b>	<b>83</b>
4.3.1 Experimental.....	83
4.3.2 Results and discussion.....	83
4.3.2.1 Spectral characteristics.....	83
4.3.2.2 Optimization of experimental conditions.....	85
4.3.2.3 Dynamic and stability.....	88

4.3.2.4 Selectivity.....	89
4.3.2.5 Calibration graphs.....	90
4.3.2.6 Discussion about the mechanism.....	91
4.3.3 Conclusion.....	93
<b>Summary</b> .....	93
<b>References</b> .....	93
Work during author's studying for Master Degree.....	94
Acknowledgements.....	95



Degree papers are in the “[Xiamen University Electronic Theses and Dissertations Database](#)”.

Fulltexts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.